(12) **UK Patent Application** (19) **GB** (11) **2 227 249**(13)**A**

(54) **Process for producing olefins from natural gas**

(57) Olefins are produced from natural gas as follows: the natural gas (2) is mainly fractionated (1) into methane (3) and higher hydrocarbons (4), the latter being then mainly fractionated (17, 20) into propane (9) and ethane (7). The methane (3) admixed with oxygen (6), passes through an oxidation reactor (5), receives the ethane (7) and the obtained mixture passes through a pyrolysis reactor (8). The effluent coming out of reactor (8) receives the propane (9) and the obtained mixture passes through a pyrolysis reactor (10). A hydrocarbon flow comprising olefins (12), more particularly ethylene and propene, is recovered.
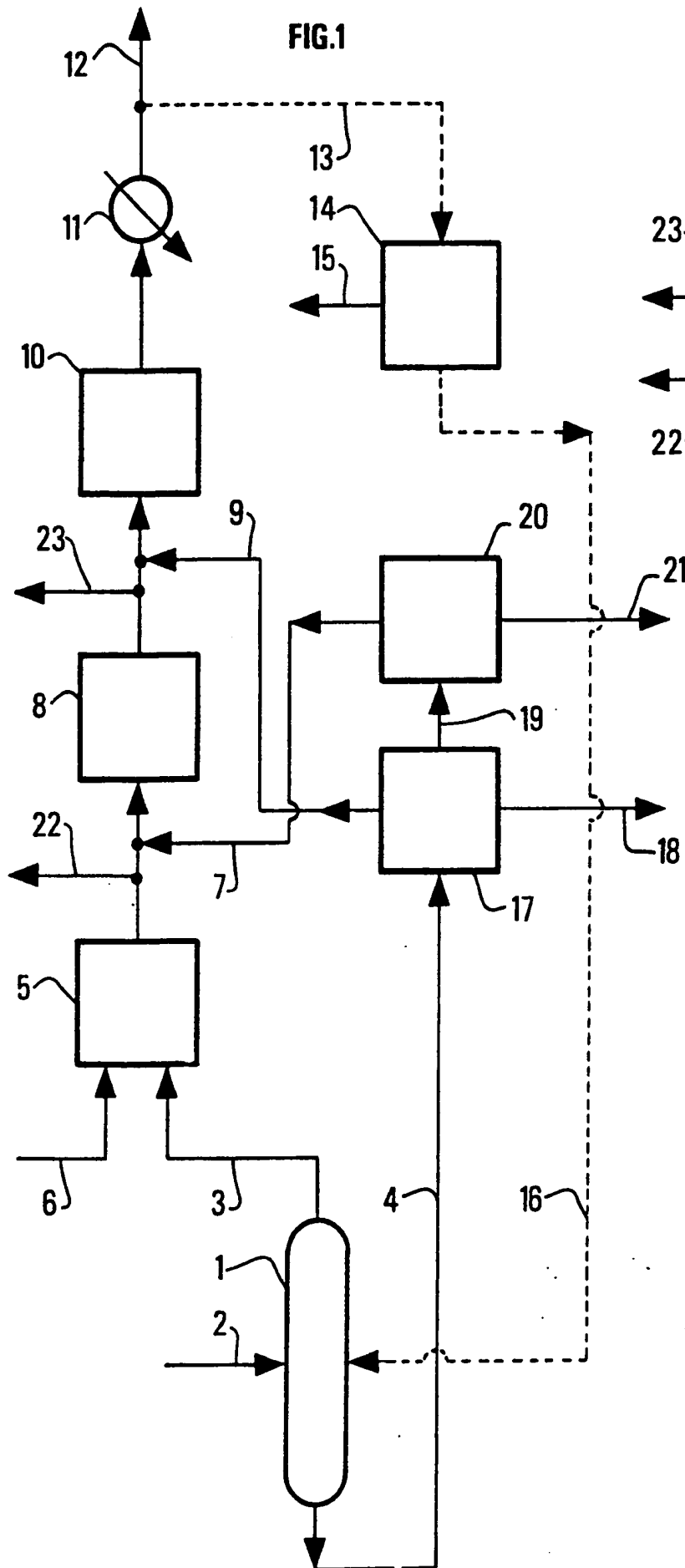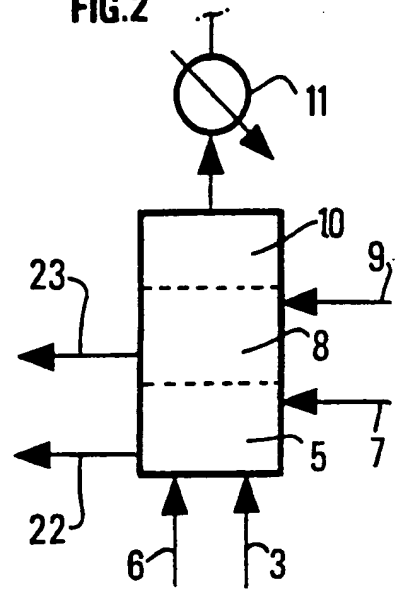
FIG.1

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PL_unique

FIG.1

FIG.2

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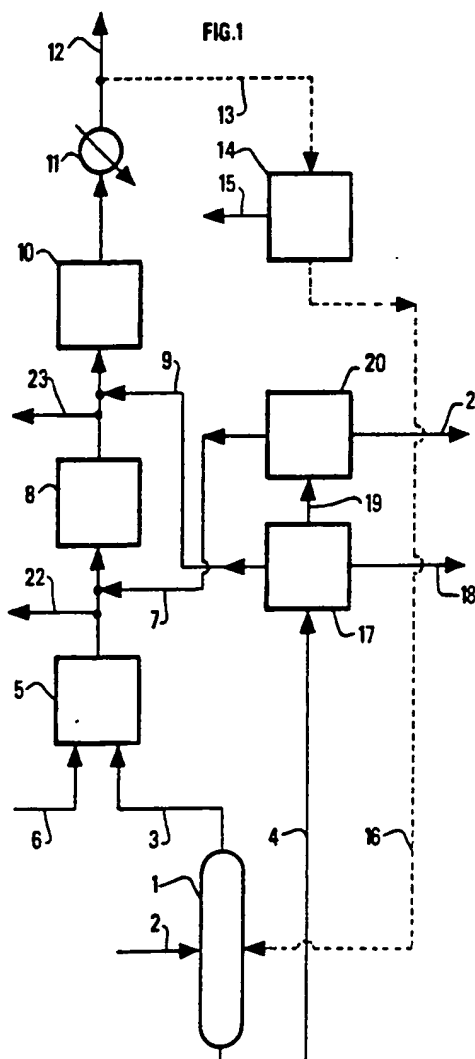
PROCESS FOR PRODUCING OLEFINS FROM NATURAL GAS

The present invention relates to a process for producing olefins from natural gas.

Natural gas is an abundant fossil raw material which is essentially composed of methane, the present proven reserves of which, about 10^{14} m^3, represent about 50 years of world consumption. Gas fields often contain considerable amounts of ethane, propane, other higher alcanes, as well as other constituents such as H_2O, CO_2, N_2, H_2S and He. The most part of the propane and of the other higher alcanes associated with natural gas are liquefied and called LPG (liquefied petroleum gas). In helium-rich fields (generally more than 0.3 % by volume), the helium is separated because of its high commercial value. The hydrogen sulfide is also separated because of its corrosive character, and the water, because of the forming of hydrates which are harmful to the transportation of natural gas. The obtained natural gas is then called non condensed gas, and it mainly contains (for example 55-99 % by volume) methane as well as ethane, generally propane and possibly low amounts of nitrogen and/or carbon dioxide.

The most part of the natural gas is used for domestic and industrial heating; however, there are some processes for converting natural gas into higher hydrocarbons.

The direct conversion of natural gas into ethylene would be a highly desirable objective, since ethylene can serve as a raw material for numerous syntheses of important products.

5   The pyrolysis and the catalytic pyrolysis of methane are both processes which allow to achieve this aim. However, these are very endothermic processes which require considerable amounts of energy. Besides, these two processes produce large amounts of non desired coke.

10   The pyrolysis of ethane is also a well-known process which is very endothermic and thus is a large energy consumer. However, as the pyrolysis of ethane is carried out at lower temperatures than that of methane, it is not possible to simultaneously convert these two compounds.
15   Thus, when it is operated at the conversion temperature of ethane, the methane which is present in the ethane-containing charge comes out of the reactor essentially unchanged.

To produce ethylene and other hydrocarbons, the
20   oxidizing coupling of methane, either in the sequential or in the simultaneous mode, has been suggested.

The reaction of the oxidizing coupling in the sequential mode consists in the oxidation of the methane by a reducible agent, followed by the re-oxidation of
25   this agent, separately, by the oxygen in the air. Several American patents (for example 4,499,323 ; 4,523,049 ; 4,547,611 ; 4,567,307) have mentioned the use of numerous

metal oxides. mainly Mn. Ce. Pr, Sn, In, Ge, Pb, Sb, Bi, Tb, as reducible agents for this reaction.

The reaction of the oxidizing coupling in the simultaneous mode (scavenging of a mixture of methane and oxygen on a contact mass) can be written qualitatively :

$$CH_4 + O_2 \longrightarrow C_2H_6 + C_2H_4 + \text{other hydrocarbons} + CO + CO_2 + H_2 + H_2O$$
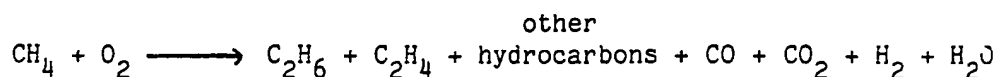
The use of rare-earth oxides, of alkaline and alkaline-earth oxides, and of titanium, zirconium, hafnium and zinc oxides, either alone or mixed , as catalysts for the reaction of the oxidizing coupling of methane in the simultaneous mode has been mentioned in several patents (for example European patents EP 210,383 A2 ; EP 189,079 A1 ; EP 206,044 A1 and world patent WO 86 07351).

It has to be noticed that the previous works concerning the oxidizing coupling of methane have led to the forming of low ethylene to ethane ratios, generally ranging from about 0.8 to 1.2 for C_2+ product selectivities higher than about 65 %. Such low ethylene to ethane ratios require the separation of ethane from ethylene and the costly pyrolysis of ethane into ethylene. Besides, the previous works on the oxidizing coupling of methane have not taken into account the other major constituents of natural gas such as ethane, propane and other saturated hydrocarbons. The processes for the

oxidizing coupling of methane described above are little appropriate for the selective conversion of natural gas into olefins because of the presence of significant amounts of light hydrocarbons (such as ethane and
5 propane) in natural gas. The relative oxidation velocities of light alcanes in the conditions of the oxidizing coupling of methane are about 15 to 100 times higher than those of the oxidation of methane, that is to say that the light hydrocarbons are converted into
10 ethylene and carbon oxides before the methane begins to react. Thus, the previous processes cannot be efficiently applied to natural gas.

Considering the sometimes appreciable presence of propane, possibly of other light alcanes in natural gas
15 and possibly of light hydrocarbons from other units located for example close to the natural gas oxipyrolysis unit, it is very advantageous to upgrade, besides the methane and the ethane, the propane and possibly other higher alcanes.

20

Thus, one object of the present invention is to provide a method for producing olefins, mainly ethylene and propene, with a high yield, from natural gas.

Another object of the present invention is to
25 provide a method for the dehydrogenation of the alcanes coming out of the methane oxidation reactor without requiring an independant pyrolysis reactor.

These objectives are reached by the present process of oxipyrolysis of natural gas which comprises the following stages :

5   (1) separation of the natural gas into two fractions: a first gas fraction enriched with methane (which is preferably substantially free from ethane, propane and other hydrocarbons associated with natural gas) and a second gas fraction enriched with hydrocarbons

10   higher than methane (particularly ethane and propane, and which may or not also contain non hydrocarbon gases) ;

(2) selective oxidation of the first methane-containing gas fraction by molecular oxygen, in the presence of a contact mass, to form an effluent

15   containing C_2 hydrocarbons and water as main products ;

(3) separation of the second gas fraction enriched with hydrocarbons higher than methane into two new fractions : a first propane-enriched gas fraction and a second ethane-enriched gas fraction ;

20   (4) addition of the second ethane-enriched gas fraction from stage (3), alone or in the presence of a gas enriched with ethane that does not stem from natural gas, to the effluent from the selective oxidation reaction of methane from stage (2), in a place where at

25   least about 30 % (preferably at least about 95 %) by

volume of the molecular oxygen introduced in stage (2) have been consumed :

(5) pyrolysis of the mixture of said effluent and said second gas fraction enriched with ethane from stage (3) :

(6) addition of the first propane-enriched gas fraction from stage (3), alone or in the presence of a gas enriched with propane that does not stem from natural gas. to the pyrolysis effluent from stage (5). in a place where said pyrolysis effluent from stage (5) has an olefins/C_2+ alcanes molar ratio of at least 0.5 : and

(7) pyrolysis of the mixture from stage (6), in order to produce an olefin-rich gaseous mixture.

The process of oxipyrolysis of natural gas according to the present invention has the following main advantages :

a) the heat released during the selective oxidation reaction of the methane (approximately 250 kJ per mole of methane having reacted) is immediately used for the pyrolysis of the effluent alcanes and of the other added alcanes :

b) the sequential addition of ethane, then of propane allows to take a better advantage of this heat release :

c) appropriate olefins/alcanes ratios can be obtained by controlling the residence times in pyrolysis stages (5) and (7) and the temperature of the gaseous effluent which immediately results from the selective oxidation of the methane :

d) the effluent from the selective oxidation reaction of the methane can serve as a dehydrogenation diluent for a pyrolysis reaction of ethane and other saturated hydrocarbons which can be introduced after the initial oxidation reaction :

e) the necessity of separately converting ethane into ethylene and propane into propene by a conventional pyrolysis process is eliminated :

f) the process allows to treat the total natural gas and not only the methane contained in the natural gas; particularly the addition of propane, and possibly of other higher alcanes, after that of ethane, allows to better upgrade the C_7+ alcanes.

In relation to a process where the addition of ethane and of propane to the effluent of the methane oxidation reaction would be simultaneous, the process of the invention particularly allows to avoid a substantial conversion of the propane into propene, followed by a degradation of the propene before obtaining a high conversion rate of ethane into ethylene.

Concerning the contact mass for the selective oxidation reaction of methane into higher hydrocarbons (stage (2) of the process according to the invention), although it is possible to use any well-known contact

5 mass to do so, it is preferred to utilize a contact mass which :

a) can operate in the normal conditions of the oxidizing coupling, for example at temperatures ranging from about 650 to about 1.200°C, preferably from about

10 650 to about 950°C .

b) produces C_2+ products with a selectivity of at least about 65 % for a methane conversion rate of about 15 %. and

c) maintains its activity and its selectivity for

15 numerous operating hours.

The contact masses which correspond to the conditions above and the use of which is thus preferred are those which generally contain oxides and/or carbonates of alkaline metals (such as lithium, sodium,

20 potassium, rubidium and cesium), of alkaline-earth metals (such as beryllium, magnesium, calcium, strontium and baryum) and of rare-earth metals (such as yttrium, lanthanum, praseodymium, neodymium, samarium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium,

25 europium and lutetium), either alone (as in the case of rare-earths and alkaline-earths), or mixed (as in the case of alkaline-earth metals doped with alkaline metals

and of rare-earth metals doped with alkaline and/or alkaline-earth metals). Other contact masses which correspond to the conditions above are those that contain oxides and/or carbonates of titanium, zirconium, hafnium,

5   manganese, cerium, tin, indium, germanium, lead, antimony, zinc and bismuth, preferably with one or several oxides and/or carbonates of alkaline, alkaline-earth and rare-earth metals and silica. The contact masses cited above are efficient alone or doped with

10   halogenides. phosphorus or sulfur oxides.

It is also interesting that the contact masses for the selective oxidation of methane :

(a)   be effective for very short contact times, generally less than about 300 milliseconds.

15   (b)   be able to consume at least about 80 % (preferably at least about 95 %) by volume of the molecular oxygen in the charge during very short contact times.

The contact masses which are particularly

20   interesting are the following :

(a)   Contact masses containing alkaline-earth and rare-earth compounds and approximately corresponding to the following formula :
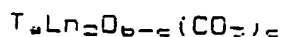
$$T_x Ln_2 O_{6-c} (CO_3)_c$$

where T represents one or several alkaline-earth metals such as beryllium, magnesium, calcium, strontium and baryum. Ln represents one or several rare-earth metals such as yttrium, lanthanum, cerium, praseodymium, neodymium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium and lutetium, a = 0.001 to 1,000 ; b = 3 + a ; c = 0.1 to b ; the preferable rare-earth metals are lanthanum, neodymium and samarium, alone or mixed ; the preferred rare-earth metal is lanthanum.

(b) Contact masses containing alkaline-earth, rare-earth and group IVA compounds and approximately corresponding to the following formula :

$$T_aM_dLn_2O_{e-f}(CO_3)_f$$

where T represents one or several alkaline-earth metals, M represents one or several metals from group IV A such as titanium, zirconium and hafnium. Ln represents one or several rare-earth metals, a = 0.001 to 1,000 ; d = 0.001 to 2 ; e = 3 + a + 2d - z ; f = 0.1 to e ; z = 0 to 0.5d ; in this formula, z represents a value from 0 to 0.5d, thus, z is equal to 0 when the oxidation state of all the metals from group IV A is +4 , 0.5d when the oxidation state of these metals is +3, and ranges from 0 to 0.5 d when there is a mixture of the oxidation states +3 and +4 of these metals ; the preferred rare-earth metals are lanthanum, neodymium and samarium, and more particularly lanthanum.

Contact masses (a) and (b) are nevertheless not limited to the formulas above. In fact. the beneficial effect of the presence of rare-earth and alkaline-earth metals and possibly of metals from group IV A appears whatever the form under which these metals are present, although the oxide and/or carbonate form is preferred.

(c) Contact masses containing two or several alkaline-earth metals and approximately corresponding to the following formula :

$$T_gT'_{2-g}O_n(CO_3)_{2-n}$$

where T represents one or several alkaline-earth metals that are different from T'. such as beryllium, magnesium, calcium, strontium and baryum. T' represents an alkaline-earth metal known for forming carbonates that are stable at high temperature, such as calcium, strontium and baryum. g = 0.1 to 1.9 . n = 0 to 2 ; the preferable T' alkaline-earth metals are strontium and baryum.

Contact masses (c) are nevertheless not limited to the formula above. In fact, the beneficial effect of the presence of at least two alkaline-earth metals (or at least one component such as calcium, strontium or baryum) appears whatever the form under which these metals are present, although the carbonate or the oxide and carbonate form is preferred.

The gas fraction subjected to the oxidation (stage (2) of the process according to the invention) can be used without a diluent or diluted by inert gases such as nitrogen, carbon dioxide or steam. For security reasons and in order to avoid too high a temperature rise, which would be harmful to the selectivity of the operation, the oxygen content in the methane can generally not exceed 40 % by mole; it can thus range from about 0.1 to 40 % by mole, preferably from about 5 to 25 % by mole.

The temperature of the oxipyrolysis reaction (stages (2), (5) and (7) of the process according to the invention) generally ranges from about 650 to about 1.200°C, preferably from about 650 to about 950°C.

The total pressure (stages (2), (5) and (7)) can for example range from about 1 to about 100 bars, and especially from about 1 to about 20 bars. The contact time of the oxidizing coupling of methane (that is the time necessary for achieving the consumption of at least about 80 % of the molecular oxygen in the charge) usually ranges from 10^{-6} to 1 second, preferably from 10^{-6} to 10^{-1} second. The total residence time in both pyrolysis sections (stages (5) and (7) of the process according to the invention) preferably ranges from about 10^{-3} to 10 seconds, and especially from about 10^{-3} to 2 seconds.

The selective oxidation of the gas fraction containing methane (stage (2) of the process according to the invention) can be implemented in any reactor type,

particularly in a fixed bed. an ebullated bed, a circulating bed or a fluidized bed reactor, preferably in a fixed bed reactor.

The following non limitative examples represent
5   embodiments which can be used for performing the oxipyrolysis of natural gas according to the invention, with the stepped addition of C_2+ saturated hydrocarbons after the stage of selective oxidation of the methane, and are illustrated by figures 1 and 2.

10   A natural gas flow (2), preferably purified (having for example been subjected to the usual dehydration, desulfurization and decarbonatation treatments), is fractionated in separator (1) into a gas fraction rich in methane (3) and a gas fraction rich in hydrocarbons
15   higher than methane (4). The flow of methane-rich gas fraction (3) is pre-heated, either alone or in the presence of steam. at a temperature which does not generally exceed about 650°C, then it is admixed with a gas rich in molecular oxygen (6) before being contacted
20   with the fixed bed in reactor (5). The contact mass (which can be present in the fixed bed in the form of a powder, granules, extrudates. pellets or supported on oxides and/or carbonates of alkaline-earth and/or rare-earth metals. on zircon, silica, alumina, quartz or on
25   monoliths such as cordierite, mullite or alpha alumina) is heated up, by the exothermicity of the oxidation reaction. at a temperature generally ranging from about 650 to about 1,200°C. The temperature of the contact mass

is a function of the initial temperature of the gas
containing the mixture of methane and molecular oxygen,
of the amount and of the enthalpy of the effluent and of
the mixture containing the methane and the oxygen and of
5   the effluent heat capacity. In the case of a reactor (5)
of the circulating or fluidized bed type, the mixture of
methane and of molecular oxygen is introduced into the
bottom of said reactor (5); this charge then draws the
hot contact mass which is driven to the top of reactor
10 (5); then, this contact mass can generally either go down
to the bottom of reactor (5), by a different way, where
it is drawn again, or be transferred outside reactor (5)
for a further treatment before being drawn again.

A flow (7) of an ethane-rich gas is then added to
15 the effluent of reactor (5), in a place where at least
about 80 % (preferably at least about 95 %) of the
molecular oxygen have been consumed.

Said ethane-rich added gas (7) can be introduced at
room temperature or pre-heated at a temperature lower
20 than the effluent temperature. In both cases, said added
gas (7) is used for lowering the effluent temperature and
it produces then a mixture which is at a temperature that
is lower than that of the effluent. The temperature of
the mixture can be controlled by adjusting the
25 temperatures of the methane charge and of said added gas
and the initial percentage of molecular oxygen. The
residence time of the mixture (of the effluent and of
said added gas) in pyrolysis reactor (8) is determined

in relation to the mixture temperature and to the desired pyrolysis severity. The pyrolysis reaction can be carried out either in the absence of a contact mass or in the presence of a contact mass such as one of those which are known for the selective oxidation of methane.

A flow (9) of a propane-rich gas is then added to the effluent of reactor (8) in a place where said effluent has an olefins/C_2+ alcanes molar ratio of at least 0.5. This flow (9) to be added can be introduced at room temperature or pre-heated at a temperature lower than that of the effluent. In both cases, said added flow (9) is used for lowering the effluent temperature and it produces then a mixture which has a temperature that is lower than the effluent temperature. Said mixture goes through pyrolysis reactor (10) where its residence time is determined in relation to its temperature and to the desired pyrolysis severity. The pyrolysis reaction can be carried out either in the absence of a contact mass or in the presence of a contact mass such as those which are known for the selective oxidation of methane or such as those which are known for the dehydrogenation of propane.

The effluent gas of reactor (10) is quenched (11) and carried off (12) if it is going to be used as it is. It is also possible to recycle it (13); it is then often

advantageous to subject said gas to various

fractionatings such as :

- drain, which allows to avoid an accumulation of gases

such as H_2 , He, N_2 or CO ;

5   - amine washing, allowing to remove CO_2 ;

- methanation, allowing to convert CO and H_2 into CH_4 and

H_2O .

These fractionatings are globally represented by

unit (14): the separated gases are removed through line

10   (15). The remaining gas, which comprises non converted

hydrocarbons, ethylene and propene, is fed into separator

(1) through line (16).

The C_2+ hydrocarbons coming from separator (1)

through line (14) are subjected to various fractionatings

15   such as, for example :

- fractionating by condensation under pressure at low

temperature, allowing to separate the C_2 , C_3 and C_4+

fractions ;

- absorption in sulfuric acid, oligomerization of the

20   olefins into liquid fuels (for example into gasoline

and/or gas oil) or dimerization reaction allowing to

separate the olefins from the C_2 , C_3 and C_4+ alcanes ;

and/or

- any combination of methods known by the man skilled in

25   the art and allowing to separate olefins from C_2 , C_3 and

C_4+ alcanes.

These fractionatings are globally represented by units (17) and (20). The gas fraction rich in C_2+ hydrocarbons from separator (1) is fed into separator (17) through line (4) : a gas fraction rich in propane is

5 separated in unit (17) and fed towards pyrolysis reactor (10) through line (9) ; a gas fraction rich in unsaturated C_3 and in C_4+ hydrocarbons is discharged from unit (17) through pipe (18) ; a gas fraction rich in C_2 hydrocarbons is separated in unit (17) and fed into

10 separator (20), through line (19), where an ethane-rich gas fraction is separated from an ethylene-rich gas fraction. The ethane-rich gas fraction is then transferred to pyrolysis reactor (8) through line (7) ; the ethylene-rich gas fraction is discharged from unit

15 (20) through pipe (18).

Lines (22) and (23) allow to take samples, especially in order to measure the conversion of the molecular oxygen and the olefins/C_2+ alcanes molar ratio.

Whatever the type of the reactors used in the

20 process according to the invention, it is possible to utilize distinct reaction sections for stages (2), (5) and (7) of said process (figure 1) or only one section comprising three successive reaction zones (figure 2).

CLAIMS

1. A process for producing olefins from natural gas containing methane, ethane and propane, characterized in that :

(1) the natural gas is separated into two fractions, a
5 first gas fraction enriched with methane and a second gas fraction enriched with hydrocarbons higher than methane.

(2) the first gas fraction enriched with methane is selectively oxidized by molecular oxygen, in the presence
10 of a contact mass, to form an effluent containing C_2 hydrocarbons and water as main products.

(3) the second gas fraction enriched with hydrocarbons higher than methane is separated into two new fractions, a first gas fraction enriched with propane and a
15 second gas fraction enriched with ethane,

(4) the second ethane-enriched gas fraction from stage (3) is admixed with the effluent from stage (2) when at least about 80 % by volume of the molecular oxygen have already been consumed in stage (2),

(5) the mixture resulting from stage (4) is pyrolyzed,

(6) the first propane-enriched gas fraction from stage (3) is admixed with the effluent from stage (5), when said effluent from stage (5) has an olefins/C_2+ alcanes molar ratio of at least 0.5 , and

(7) the mixture resulting from stage (6) is pyrolyzed.

2. A process according to claim 1 wherein the second gas fraction enriched with ethane and stemming from stage (3) is admixed, prior to stage (4), with a gas enriched in ethane which does not stem from the natural gas.

3. A process according to one of claims 1 and 2 wherein the first gas fraction enriched with propane and stemming from stage (3) is admixed, prior to stage (6), with a gas enriched with propane which does not stem from the natural gas.

4. A process according to one of claims 1 to 3 wherein, in stage (2), the oxygen proportion ranges from about 0.001 to 0.4 mole per mole of methane.

5. A process according to one of claims 1 to 4 wherein the mixture of stage (4) is carried out when at least 95 % by volume of the molecular oxygen have already been consumed in stage (2).

6. A process according to one of claims 1 to 5 wherein stages (2), (5) and (7) are carried out at a temperature ranging from about 650 to about 1,200°C and under a pressure ranging from about 1 to about 100 bars.

7. A process according to one of claims 1 to 6 wherein the contact mass of stage (2) answers the following formula : $T_aLn_2O_{b-c}(CO_3)_c$, where T represents at least one alkaline-earth metal. Ln represents at least one rare-earth metal. a = 0.001 to 1,000 ; b = 3 + a ; c = 0.1 to b.

8. A process according to one of claims 1 to 6 wherein the contact mass of stage (2) answers the following formula : $T_aM_dLn_2O_{e-f}(CO_3)_f$, where T represents at least one alkaline-earth metal, Ln represents at least one rare-earth metal. M represents one or several metals from group IV A, a = 0.001 to 1,000 ; d = 0.001 to 2 ; e = 3 + a + 2d - z ; f = 0.1 to e ; and z = 0 to 0.5d.

9. A process according to one of claims 1 to 8 wherein the effluent from stage (7) is fractionated in order to remove the carbon dioxide, then it is subjected to a methanation and finally the resulting gaseous effluent is fed back to stage (1).

10. A process according to one of claims 1 to 9 for producing ethylene and propene.

11. A process according to Claim 1, carried out in apparatus substantially as hereinbefore described with reference to the accompanying drawings.

Amendments to the claims have been filed as follows

6.   A process according to one of Claims 1 to 5 wherein stages (2), (5) and (7) are carried out at a temperature ranging from about 650 to about 1.200°C and under a pressure ranging from about 1 to about 100 bars.

5

7.   A process according to one of Claims 1 to 6 wherein the contact mass of stage (2) answers the following formula: $T_aLn_2O_{b-c}(CO_3)_c$, where T represents at least one alkaline-earth metal, Ln represents at least one rare-earth metal, a = 0.001 to 1.000; b = 3 + a; c = 0.1

10   to b.

8.   A process according to one of Claims 1 to 6 wherein the contact mass of stage (2) answers the following formula: $T_aM_dLn_2O_{e-f}(CO_3)_f$, where T represents at least one alkaline-earth metal, Ln represents at

15   least one rare-earth metal, M represents one or several metals from group IV A, a = 0.001 to 1.000; d = 0.001 to 2; e = 3 + a + 2d - z; f = 0.1 to 3; and z = 0 to 0.5d.

9.   A process according to one of Claims 1 to 8 wherein the effluent

20   from stage (7) is fractionated in order to remove the carbon dioxide, then it is subjected to a methanation in order to convert carbon dioxide and hydrogen into methane and water and finally the resulting gaseous effluent is fed back to stage (1).

25   10.   A process according to one of Claims 1 to 9 for producing ethylene and propene.

11.   A process according to Claim 1, carried out in apparatus substantially as hereinbefore described with reference to the

30   accompanying drawings.